Viscosity of bulk metallic glass forming liquids close to the liquidus temperature.

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ABSTRACT
The viscous properties of multi component bulk metallic glass forming alloys were studied above the liquidus temperature. A shear thinning behavior for the molten alloy has been discovered. The shear thinning behavior can be characterized as a power law fluid with a power-law index of -1/2. High purity carbon graphite crucibles were used as the shear cell material. The shear cell was contained within a high vacuum chamber capable of absolute pressures less than 10^{-6} mbar. An induction power supply with a power output of 15kW was used to heat the shear cell and sample material. Over the length of the test temperature fluctuations of less than ±1K were attained.

INTRODUCTION
Viscometric properties of bulk metallic glass have scientific and technical importance. Understanding the response to an applied stress as a function of time at various temperatures gives important details about the material, such as kinetic and thermodynamic properties [1]. Additionally, the viscometric properties are important when processing from the melt. Due to the relatively high critical cooling rates and temperatures, the viscosity of the material as a function of temperature becomes a key factor when designing and processing for bulk metallic glasses.

Previous viscosity measurements of bulk metallic glasses have been primarily focused in the undercooled region, typically near the glass transition temperature. Typical measurement methods used for these temperatures are beam bending, parallel plate [2, 3, 4,5]. These techniques are capable of measuring viscosity on the order of 10^5-10^{14} Pa*s. Above the liquidus temperature viscosity measurements have been made using methods such as oscillating drop [3] and rotating concentric cylinder [5, 6]. Previously it has been shown that at the liquidus temperature bulk metallic glass forming alloys have a viscosity on the order of 10^2 Pa*s, as compared with pure metals which have a viscosity on the order of 10^{-3} Pa*s. It is important to note that previous viscosity measurements above the liquidus temperature for bulk metallic glasses have not studied the effect of varying shear rate.

EXPERIMENTAL
For measuring the flow properties of bulk metallic glass above the liquidus temperature a high temperature rheometer was designed, built and calibrated. Due to the high reactivity of the molten alloys the shear cell of the rheometer was contained within a vacuum chamber, as seen in Figure 1. Prior to testing the rheometer chamber is purged with high purity Argon (99.999%). During testing the viscometer is maintained at absolute pressures $<10^{-5}$ mbar. The power into the shear cell is provided by an induction power supply capable of a maximum output of 15kW. The power supply is controlled by the user via a personal computer outfitted with a data acquisition card and a custom software program. The data acquisition card is available from National Instruments, and the custom software program was written using LabView again available from

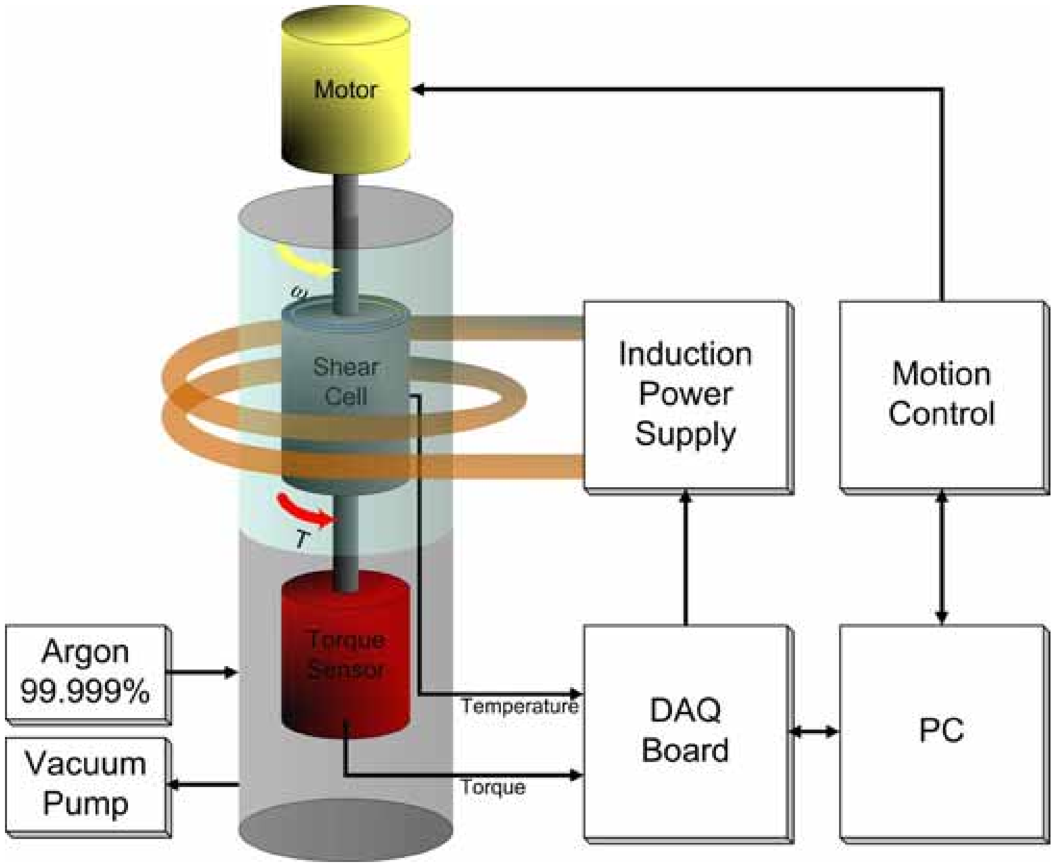

Figure 1: Schematic of the high temperature high vacuum rheometer built for the investigation of bulk metallic glass forming alloys.

National Instruments. Additionally, the computer controls the rotational frequency and measures the temperature and the torque on the shear cell. The computer stores the time, temperature, torque, and rotational frequency information on the hard drive for post processing.

The rheometer is a Searle type utilizing the flow between concentric cylinders. In a Searle type rheometer the inner cylinder rotates while the torque in measured at the outer cylinder. The current configuration for the rheometer is capable of rotational velocities from $9.42*10^{-3}$ to $3.77*10^{1}$ radians/s.

The rheometer has been temperature calibrated between 292.65 and 304.15 K for room temperature measurements and between 1234.93 and 1357.77 K. The low temperature calibrations were performed using a NIST traceable RTD available from Omega Engineering and a temperature controlled water bath. The high temperature calibrations were performed using the melting points of Al, Ag, and Cu in high purity carbon crucibles (Poco Graphite, DFP1). The purity of the metals used for calibration ranged from 99.99-99.999% pure.

In addition, isothermal viscosity calibrations were performed at 25 C using silicone fluids available from Brookfield Engineering. These fluids are NIST traceable and are known to be Newtonian at the shear rates used. The rheometer was calibrated at the following viscosities: $9.6*10^{-3}$, $9.9*10^{-2}$, $9.6*10^{-1}$, $1.188*10^{1}$, and $1.024*10^{2}$ Pa*s.

Samples of $Zr_{41.2}$ $Ti_{13.8}$ $Cu_{12.5}$ $Ni_{10.0}$ $Be_{22.5}$ (Vit 1) were obtained from Liquidmetal Technologies. Using the specific volume of Vit 1 [7] at the test temperature the sample was weighed and cleaned. Prior to performing the test the carbon shear cell was heated to approximately 1475 K for a minimum of 60 min at an absolute pressure of less than 10^{-5} mbar to assure no contamination of the molten liquid from contaminates within the carbon.

RESULTS

In Figure 2 the viscosity of the molten alloy is plotted as a function of the shear rate held at an isothermal temperature of 1115 K. From this plot it can be seen that there is a shear rate dependence to the viscosity. For a Searle type rheometer the shear stress is calculated as:

$$\sigma = \frac{C}{2\pi R_o^2 L} \qquad (1)$$

where C is the measured torque, R_o is the radius of the outer cylinder, L is the liquid contact length on the inner cylinder. The shear rate is calculated:

$$\dot{\gamma} = \frac{R_o \Omega}{R_o - R_i} \qquad (2)$$

where Ω is the rotational frequency and R_i is the radius of the inner cylinder. The viscosity becomes:

$$\eta = \frac{\sigma}{\dot{\gamma}} = \frac{C(R_o - R_i)}{2\pi R_o^3 \Omega L} \qquad (3)$$

Equation 3 is based upon a linear velocity profile of the fluid being sheared. However due to the shear thinning, as seen in Figure 2, and the shear cell geometry—the velocity profile is no longer linear. It has been shown that for a power-law fluid a corrected shear rate can be calculated using a correction factor [8, 9]. The correction factor, n, is determined by plotting the rotational frequency versus the measured torque and calculating slope of this line. This is equivalent to determining a power-fit for the torque as a function of the rotational frequency. This has been

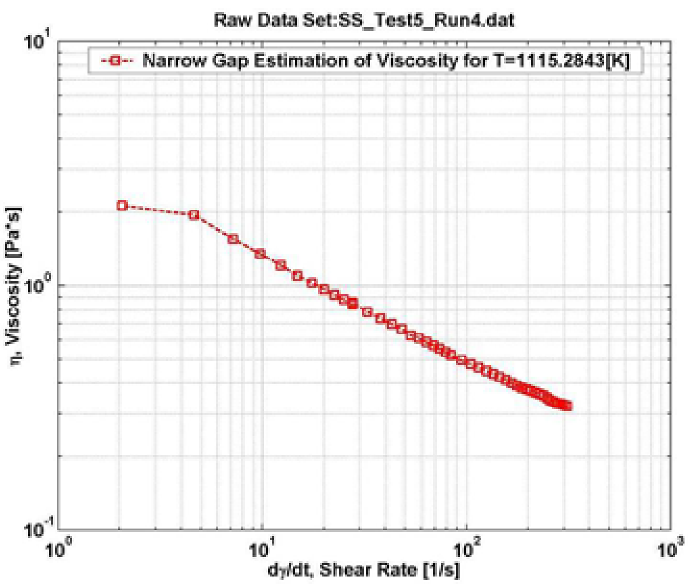

Figure 2: Plot of viscosity vs shear rate. This curve is and example of sear thinning in Vit 1.

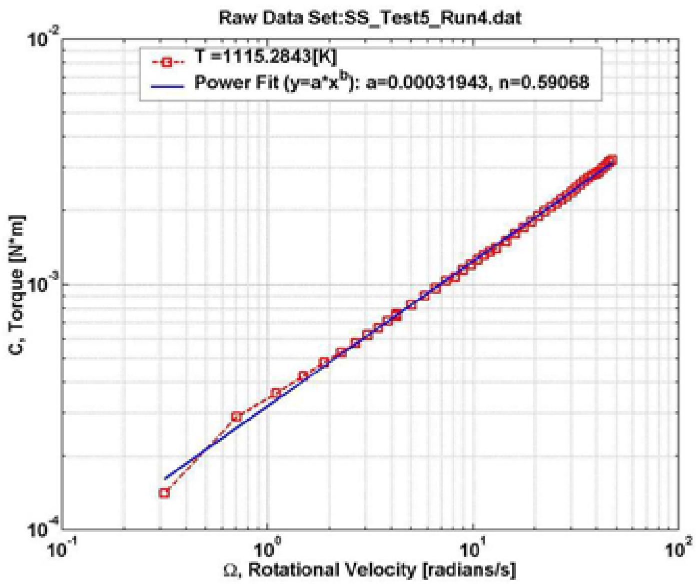

Figure 3: Measured torque vs rotational frequency for the sample of Vit 1 sown in figure 2, additionally the power law curve fit has been superimposed with correction factor n =.59.

performed on the data seen in Figure 2, and can be viewed in Figure 3 along with the line representing the power-fit to the data. Once the correction factor is determined a corrected viscosity can be calculated as:

$$\dot{\gamma}_{R_i} = \frac{2\Omega}{n(1-k^{2/n})} \tag{4}$$

where k is the ratio of the inner and outer cylinders. Using the corrected shear rate and the calculated shear stress from, equation 1, a corrected viscosity can be determined as:

$$\eta_c = \frac{\sigma}{\dot{\gamma}_{R_i}} = \frac{Cn(1-k^{2/n})}{4\pi R_o^2 L\Omega} \tag{5}$$

This correction was performed for each test. Figure 4 shows the shear stress and the corrected viscosity versus corrected shear strain for each test performed. For Figure 4b a power-law

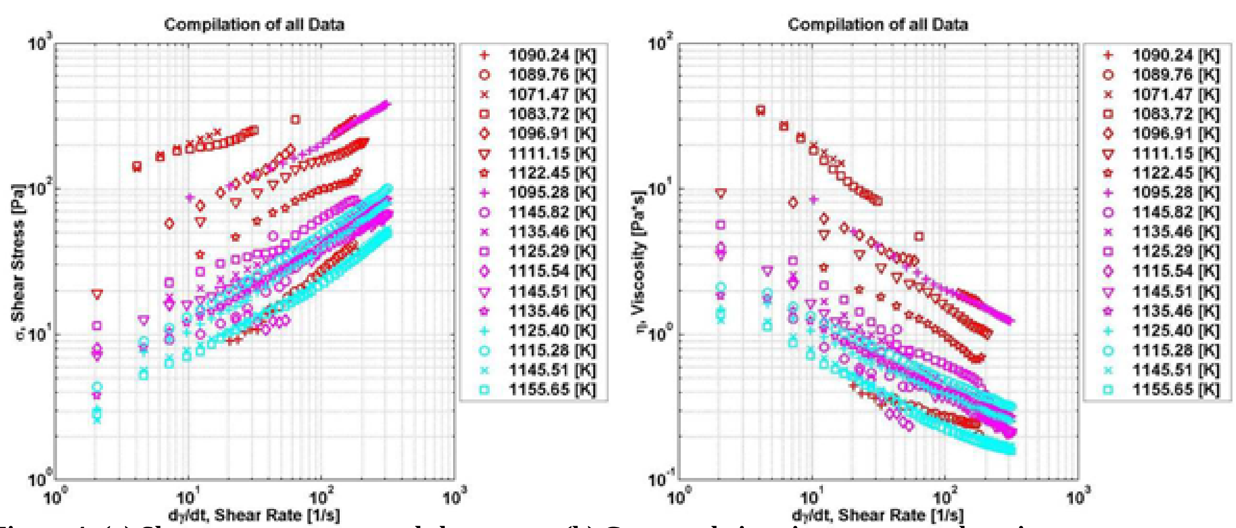

Figure 4: (a) Shear stress vs corrected shear rate. (b) Corrected viscosity vs corrected strain rate.

relationship was used to determine the dependence of the shear rate on the viscosity, otherwise know as the power-law index. It was found that the power law index for all of the data collected was -.516 with a standard deviation of .151.

In Figure 4b at higher temperatures and lower shear rates there appears to be a 'knee' in the viscosity curve. It appears that at this knee there is a change in the viscosity and the viscosity becomes less a function of the shear rate i.e. the viscosity becomes Newtonian like. In an attempt to investigate the phenomenon near the 'knee' changes were made to the physical setup to attain smaller values of shear rate. Tests were performed at lower shear rates, upon performing these tests another interesting behavior appeared, visco-elasticity. As the temperature and the shear rate were reduced the torque no longer tracked the shear rate, this can be seen in Figure 5. It is important to note that the time dependent behavior seen in Figure 5b was not included in the previous data or discussion.

DISCUSSION

From our experiments we have seen some rather interesting rheological behavior for Vit 1. Above the liquidus temperature we see two interesting phenomena shear thinning and a visco-elasticity. Due to the high temperatures it is not expected to see these types of behavior. It has been previously reported that the time scale for viscous flow for Vit 1 at the liquidus temperature should be on the order of 10^{-8} seconds [10]. It is hypothesized by the authors that the shear rate dependence of viscosity is due to the breaking up of small clusters contained within the molten alloy. Theses clusters are the result of short range ordering within the melt. Due to the reduction in viscosity with increasing shear rate it appears that the fragility increases with increasing shear rate.

To see if the shear thinning effect was an isolated characteristic for Vit 1 additional tests were performed on a titanium rich zirconium based metallic glass, LM010, also provided by Liquidmetal Technologies. This material, LM 010, also showed a shear rate dependence to the viscosity.

As the shearing action increases diffusion cannot keep up with the shearing action and the clusters reduce in size—decreasing the resistance to a shearing action. If the shearing action is

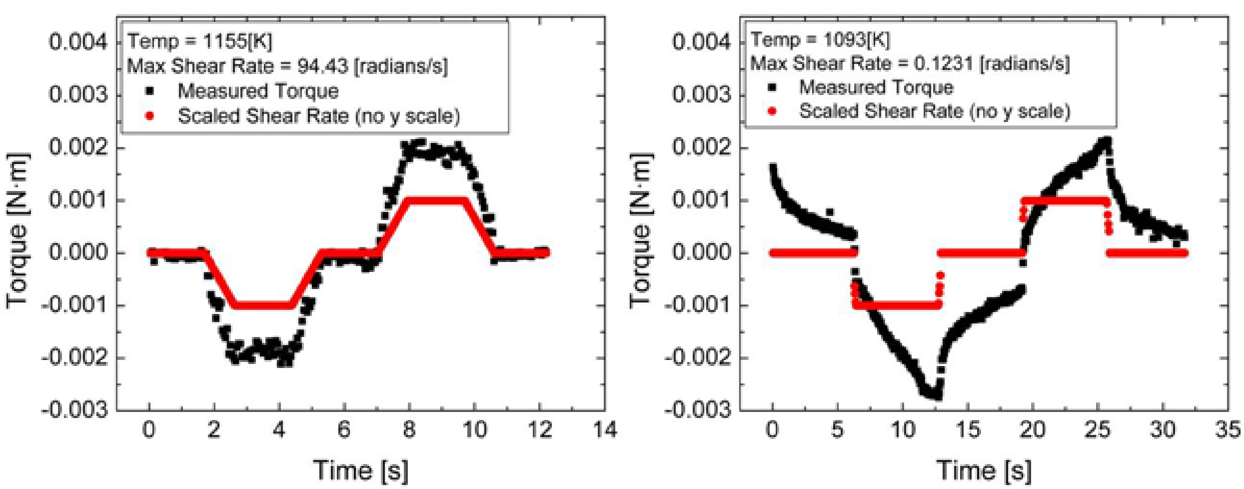

Figure 5: (a) Viscous only behavior of Vit 1, note the torque tracks the shear rate with time. (b) Visco-elastic behavior of Vit 1, note the exponential type response for the measured torque as a function of time

ceased and the temperature reduced the clusters get larger in size. Upon resuming shearing, at low magnitudes, the large clusters frequently interact with one another. At low shear rates these large clusters are mobile enough not to break up, rather change in shape increasing their energy. It is believed that this increase in energy is related to the elastic component in the visco-elastic response.

CONCLUSIONS

A high temperature high vacuum rheometer capable of measuring the viscous properties of bulk metallic glass forming alloys has been built, designed, and tested. Above the liquidus temperatures zirconium based metallic glasses have been shown to have interesting flow behaviors. At shear rates in the range of 10^0 to 10^3 s^{-1} Vit 1 has a viscosity which is well defined by a power-law type relationship with a power law exponent of approximately -.5. At lower shear rates there appears an elastic component to the flow response. Determining the flow behavior at a range of shear rates and temperatures is an ongoing investigation.

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REFERENCES

1. R. Busch, W. Liu, and W. L. Johnson, J. of Appl. Phys. **83** (8), 4143-4141 (1998)
2. R. Busch, E, Bakke, and W. L. Johnson, Acta Mater. **46** (13), 4725-4732 (1998)
3. S.C. Glade and W. L. Johnson, J of Appl. Phys. **87** (10), 7249-7251 (2000)
4. T. A. Waniuk, R. Busch, A. Masuhr, and W. L. Johnson, Acta Mater. **46** (15), 5229-5236 (1998)
5. A. Masuhr, R. Busch, and W. L. Johnson, Mater. Sci. Forum **269-272**, 779-784 (1998)
6. A. Masuhur, PhD Thesis, California Institute of Technology, 1999
7. K. Ohsaka, S. K. Chung and W.K. Rhim, Appl. Phys. Lett. **70** (6), 726-728 (1997)
8. I. M. Krieger and S.H. Maron, J. of Appl. Phys. **25** (1), 72-75 (1954)
9. H. A. Barnes and K. Hutton, *Introduction to Rheology*, 1st ed., (Elsevier Science, Amsterdam, 1998) p. 28
10. A. Masuhr, R. Busch, and W. L. Johnson, Physical Rev. Lett. **82** (11), 2290-2293 (1999)